

***Ab initio* study on the Herzberg-Teller effect in the optical excitation spectrum of silicon-vacancy center in diamond**

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Understanding optical excitation spectra of point defects is still a scientific challenge. We demonstrate by *ab initio* calculations that a prominent sharp feature in the photoluminescence (PL) spectrum of the negatively charged silicon-vacancy defect in diamond can be only explained within the Herzberg-Teller approximation that goes beyond the commonly applied Franck-Condon approximation. The effect of the dynamic Jahn-Teller effect on the PL spectrum is also discussed. Our implementation of Herzberg-Teller theory paves the way for full *ab initio* description of the optical excitation spectrum of point defects in solids.

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One of the most important fingerprints of point defects in solids is the excitation energy and the corresponding lineshape of their optical excitation spectrum. Generally, the lineshape originates from the coupling to lattice vibrations. Accurate calculation of the lineshape can serve as a tool for identification of the unknown absorption or luminescence center in solids [1]. While model calculations have been performed for quite some time [2], one can now apply accurate methods based on density functional theory (DFT) to study specific defects without any prior assumptions regarding the coupling to the lattice [3–5]. Understanding the optical excitation spectrum of point defects has recently received renewed attention because luminescent defects may act as single photon emitters [6] and/or qubits [7, 8] where in-depth knowledge about their photo-excitation spectrum is crucial to realize identical emitters.

A prominent example is the silicon-vacancy (SiV) center in diamond. SiV center has a relatively sharp zero-phonon line (ZPL) in ultrapure and strain-free diamond samples where about 30% of the luminescence appears in the phonon sideband [9–12]. The sharp ZPL makes possible to produce nearly identical emitters in different diamond samples [13, 14]. An additional advantage of SiV center is that it possesses inversion symmetry (see Fig. 1). As a consequence, it couples weakly to the external electric field, so it has virtually no spectral diffusion due to the Stark effect caused by the nearby charged defects induced by the laser that is applied to photo-excite the SiV center. This motivated us to study the phonon sideband of SiV center in great detail. Particularly, it was found that a sharp feature appears in the phonon sideband of the PL spectrum with a highest intensity of about 3% that exhibits a very sensitive Si isotope shift [15] implying that the Si-atom dominantly participates in this particular vibration mode. Since Si-atom sits in the inversion center of the defect the vibrations of Si atom

belong to the odd-parity ungerade u modes. However, the u modes are strictly forbidden to participate in the photo-excitation process according to the commonly applied Franck-Condon approximation [16, 17] because they would break the parity selection rule.

Employing density functional theory, we show in this Letter that the sharp feature in the PL phonon sideband of the SiV center in diamond, i.e., negatively charged SiV defect, cannot be explained within Franck-Condon approximation. We developed a theory based on Herzberg-Teller approximation going beyond the Franck-Condon approximation, and implemented this theory to calculate the intensity of the vibration modes in the PL spectrum. We find good agreement with the experimental data which implies that the Herzberg-Teller approximation should be invoked, in order to fully understand the PL lineshape of SiV center in diamond. We demonstrate that the largest contribution in the phonon sideband comes from the non-symmetric and degenerate even-parity gerade g phonons due to the dynamic Jahn-Teller nature of the defect.

We apply supercell plane wave DFT method to model the defect with the usual Born-Oppenheimer approximation. Most of the calculations are carried out in a 512-atom supercell within Γ -point approximation that provides convergent charge density of the system. In our simulations, we apply VASP 5.3.5 plane wave code [18] within projector-augmentation-wave-method (PAW) [19, 20]. We utilize the standard PAW-potentials and a convergent plane wave cutoff of 420 eV. We apply a very stringent upper limit of 10^{-4} eV/Å for the forces in the geometry optimization. For the calculation of the phonon spectrum we generate the dynamical matrix via finite differences of total energies. The excitation energies are calculated by constrained-occupation DFT method (CDFT). The ZPL energy is calculated by geometry optimization in the excited state within CDFT procedure.

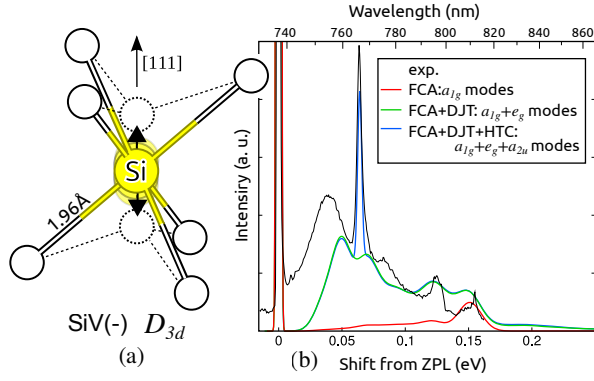


FIG. 1. (Color online) (a) Geometry of the SiV center. The arrows show the motion of Si-atom of a_{2u} vibration. (b) Low temperature experimental (black curve) and simulated photoluminescence spectrum at different level of theory: Franck-Condon approximation (FCA: red curve with a_{1g} phonons), FC with dynamic Jahn-Teller effect (FCA+DJT: green curve with e_g phonons), FC+DJT with Herzberg-Teller correction (FCA+DJT+HTC: blue curve with a_{2u} vibration). In the simulations the width of the zero-phonon line (ZPL) is taken from the experimental data. The position of the a_{2u} mode is also taken from the experiment for the sake of clarity. See the main text for details.

The electronic structure is calculated using HSE06 hybrid functional [21, 22] within DFT. Using this technique, it is possible, in particular, to reproduce the experimental band gap and the charge transition levels in Group-IV semiconductors within 0.1 eV accuracy [23]. Indeed, HSE06 provides excellent results for the ZPL energy of SiV center in diamond [24, 25].

The calculation of phonon spectrum within HSE06, however, is very expensive and intractable even on supercomputers. To obtain vibrational frequencies of HSE06 quality we used the method described and tested in Ref. [5]. In particular, we constructed the dynamical matrix for the SiV center using the fact that this matrix is rather short-ranged in diamond, allowing us to cut-off matrix elements for atoms separated more than a certain distance. The procedure is described in more detail in Ref. [26]. We compared the approach to the vibrational spectrum calculated directly for 216 and 512-atom supercells with a PBE DFT functional [27]. We find that PBE and HSE06 vibrational spectra agree very closely. In particular, the difference of energies of quasi-local modes (see below) is smaller than 2 meV. The largest difference comes from the description in bulk phonons, as for the highest-energy phonon PBE gives a value 162 meV, while HSE06 yields 167 meV, a bit closer to the experimental result of 165 meV.

The geometry and electronic structure of SiV center in diamond was already discussed in our previous study [25]: this defect can be described as a divacancy with 6 carbon dangling bonds where the Si-atom sits at the inversion center of the defect. The relevant charge state is

$q = -1$ with seven active electrons. In the ground state, 2E_g , an e_g state appears in the gap and it is occupied by three electrons. In addition, there is a fully occupied e_u state is resonant with the valence band. The excited state, 2E_u , can be constructed by promoting an electron from the e_u level to the e_g level in the gap [12, 25]; the PL process corresponds to $E_u \rightarrow E_g$ transition that is optically allowed as the parity of the wavefunctions changes. However, both the excited state E_u and the ground state E_g are Jahn-Teller-unstable. HSE06 functional with Born-Oppenheimer approximation predicts C_{2h} distortion from D_{3d} symmetry in both the ground and excited state [25]. However, detailed study on the measured optical spectrum indicates [28] that the system exhibits D_{3d} symmetry both in the ground and excited state implying a dynamic Jahn-Teller (DJT) effect. We study this in detail for the ground state in a 512-atom supercell by HSE06 calculations. We find that the energy gain by $D_{3d} \rightarrow C_{2h}$ reconstruction is 40 meV and the barrier energy for reorientation between the symmetrically equivalent C_{2h} configurations is only 10 meV which explains DJT for SiV center. We emphasize though that the C_{2h} dynamic distortion still preserves the inversion center of the defect.

We next study the phonons and quasi-local vibration modes of the SiV center. In order to enforce the effective high D_{3d} symmetry, the e_g defect level is evenly occupied in the spin minority channel in the calculation of the phonon spectrum. Vibrational analysis was performed for supercells up to 4096 atoms [26], as was previously explained for the NV center in diamond [5]. Since the DJT effect preserves inversion symmetry, it is e_g phonons that are responsible for it. Surprisingly our inverse participation ratio (IPR) analysis [26] shows that no quasilocal vibration e_g modes occur. Rather, a collective set of e_g phonons results in the DJT distortion. The breathing type of a_{1g} phonons are also all delocalized, as are a_{2g} and a_{1u} vibrations [26].

IPR analysis indicates that only a_{2u} and, to a lesser extent, e_u modes produce quasilocal (QL) vibrational modes [26]. In the QL a_{2u} mode the Si-atom moves along the C_3 axis of the defect around the inversion center with dynamically preserved C_{3v} symmetry. In the QL d_u modes the Si-atom moves perpendicular to the C_3 axis with lowering the symmetry to C_1 but the localization of e_u modes (see Supplementary Material [26]) is about an order magnitude smaller than that of the a_{2u} mode. Thus, we focus on the a_{2u} mode. It was already suspected that an a_{2u} was responsible for the sharp feature in the PL spectrum because the motion of the Si atom is needed to introduce Si-related isotope shifts in the phonon sideband of the PL spectrum observed in Ref. [15]. The calculated energy of the a_{2u} mode is 43 meV which may only broadly agree with the sharp feature at ~ 60 meV in the PL spectrum. We note that the calculated vibration energy had a reference with respect to

the D_{3d} potential energy surface but the defect is a dynamic Jahn-Teller system with a motional average D_{3d} configuration where the reference energy is not known. Thus, the exact calculation of the energy of this vibration mode is much more challenging than those in a less complicated system, such as the NV center [5]. In any case, the possible agreement of the calculated QL a_{2u} vibration frequency with the energy position of the sharp feature in the PL spectrum w.r.t. ZPL energy would not be a sufficient for identification because the a_{2u} vibration mode should be forbidden in the PL process in the first order as it breaks the parity selection rule. In order to study this effect in detail we calculated the PL lineshape from first principles as explained below.

Generally, within the Born-Oppenheimer approximation the luminescence lineshape is given via

$$A(E) \sim \sum_{m,n} w_n |\langle \chi_n^e(Q) \Psi^e(Q, r) | e \vec{r} | \chi_m^g(Q') \Psi^g(Q', r) \rangle|^2 \delta(E - E_n^e + E_m^g), \quad (1)$$

where $\chi_n^{\{e,g\}}(Q) \Psi^{\{e,g\}}(Q, r)$ is the total wavefunction in the excited (e) and ground (g) state, E_n^e and E_m^g are their corresponding total energies, and $e \vec{r} \equiv \vec{P}$ is the dipole operator. $\chi_n(Q)$ is the phonon wavefunction with the harmonic oscillator quantum number n and normal coordinate Q and $\Psi(Q, r)$ is the electron wavefunction. w_m is thermal occupation factor of the state n . In practice, our DFT calculations are valid at $T=0$ K so we compare our DFT results with the cryogenic temperature PL spectrum. In this case we restrict to $n = 0$, i.e., the zero-point-energy phonon state in the electronic excited state. Still, Eq. 1 is too complicated to solve, thus further approximations are needed. First, it can be realized that χ does not depend explicitly on r . By assuming that the integral $\vec{P}(Q, Q')$ is a constant vector $\vec{\alpha}$, i.e., the dipole transition moment does not depend on the (dynamic) motion of the ions,

$$\vec{P}(Q, Q') = \langle \Psi^e(Q, r) | e \vec{r} | \Psi^g(Q', r) \rangle \approx \quad (2)$$

$$\langle \Psi^e(r) | e \vec{r} | \Psi^g(r) \rangle = \vec{\alpha}, \quad (3)$$

then Eq. (1) is simplified to

$$A(E) \sim \alpha^2 \sum_m |\langle \chi_0^e(Q) | \chi_m^g(Q') \rangle|^2 \delta(E - E_0^e + E_m^g). \quad (4)$$

This is often called the Franck-Condon spectrum and the $|\langle \chi_0^e(Q) | \chi_m^g(Q') \rangle|^2$ overlaps are the Franck-Condon factors. The ZPL transition belongs to $m = 0$ in Eq. (4) whereas the phonon sideband comes from $m > 0$ overlap integral. In general, Franck-Condon factors are highly multidimensional integrals, and in order to calculate them further approximations are needed. We will thus assume that both vibrational modes and their frequencies are the same in the ground and the excited state [2].

Our explicit calculations of the vibrational spectrum in the excited state shows that this is a very good approximation. In this case the multi-dimensional integral factorizes into many one-dimensional integrals, significantly reducing the computational cost. The coupling to a vibrational mode k during optical transition is described by a partial Huang-Rhys [29], which describes how many phonons of type k are on average generated during the transition. Given these partial Huang-Rhys factors, the luminescence lineshape is then computed using the generating function approach [30, 31] (see, e.g., Eqs. (4)-(11) in Ref. [5]). When both the excited state and the ground state possess D_{3d} symmetry, only fully symmetric a_{1g} vibrations yield non-zero overlap integrals within the Franck-Condon approximation.

The resulting spectrum, which models the contribution of a_{1g} vibrations in the overall spectrum, is shown in Fig. 1(b). Coupling to a_{1g} phonons contributes to a resonance at around 160 meV; otherwise it produces a broad spectrum. We find that the intensity of the phonon sideband is only 5% w.r.t. the intensity of ZPL in the PL spectrum. This contradicts with the experimental value of about 32% and since the sharp feature only contributes by $\approx 3\%$, thus a_{1g} phonons cannot account for the missing broad phonon bands. Here we have to consider the DJT nature of the defect. In the DJT solution the electron and phonon states are coupled: it may be expressed in a Born-Oppenheimer basis as a linear combination of $\chi\Psi$ functions resulting in polaron wavefunctions and polaron eigenenergies. Since e_g phonons participate in the DJT process they may appear in the PL spectrum as the polaron wavefunction transforms as $E_g \times e_g$ that contains the fully symmetric A_{1g} . Recent study has shown [32] that many-body perturbation theory (MBPT) on electron-phonon coupling may be applied for accurate calculation of the spectral functions of polaron-like states that appear in DJT systems. This is beyond the scope of this Letter. Nevertheless, an approximate solution may be found in our 512-atom supercell calculations by using the fact that (i) the ground and excited state shows very similar distortion, i.e., very similar potential energy surfaces, (ii) the JT coupling is relatively small as the calculated energy of reconstruction (40 meV) is comparable to the average energy of the e_g modes (~ 100 meV) responsible for the distortion.

Based on these considerations we calculate the contribution of e_g modes in the PL spectrum between displaced harmonic oscillators of C_{2h} configurations in the 512-atom supercell [see Fig. 1(b)]. We obtain $\approx 30\%$ contribution to the phonon assisted bands. This strongly suggests that e_g phonons are mostly responsible for the broad phonon sidebands in the PL process because of the DJT effect. The coupling produces features at around 40, 120 and 160 meV that are visible in the experimental PL spectrum. We note that the low energy part is not well reproduced. According to our recent result, the fine

structure of polaronic DJT system may be described by a convolution of MBPT and Huang-Rhys methods [32] that should be combined with an embedding procedure [5], in order to calculate the low energy acoustic phonons. That issue is beyond the scope of the present study focusing on the presence of a_{2u} mode in the PL spectrum. Nevertheless, we can conclude that the broad features in the PL phonon sideband dominantly arise from the degenerate e_g phonons due to DJT effect.

Now we turn the analysis of the QL a_{2u} mode that might cause the sharp feature in the PL spectrum at ~ 60 meV. We calculated the potential energy surface around D_{3d} geometry along the normal coordinate of the QL a_{2u} mode: it shows a harmonic potential. We conclude that the Born-Oppenheimer approximation should hold for the a_{2u} mode but the Franck-Condon approximation in Eq. 2 should fail. Now, we modify this equation where we fix the normal coordinate at the electronic ground state ($Q \approx Q'$, equilibrium geometry being $Q = 0$),

$$\vec{P}(Q) = \langle \Psi^e(Q, r) | e \vec{r} | \Psi^g(Q, r) \rangle \approx \vec{\alpha} + \vec{\beta} Q. \quad (5)$$

Here, the dynamic motion of the atoms may result in change in the strength of the optical transition. This may be considered as a linear expansion ($\vec{\beta}$) within the Herzberg-Teller theory. If we insert Eq. 5 into Eq. 1 then it leads to

$$A(E) \sim \alpha^2 \sum_m (|\langle \chi_0^e(Q) | \chi_m^g(Q) \rangle|^2 + \beta^2 |\langle \chi_0^e(Q) | Q | \chi_m^g(Q) \rangle|^2) \delta(E - E_0^e + E_m^g). \quad (6)$$

The first term in the sum of Eq. 6 is what we obtain in the usual Franck-Condon approximation (in the limit of $Q \approx Q'$) whereas the second term is the Herzberg-Teller correction [1]. Here we assume that the second term is important to consider only for those vibration(s), i.e. the a_{2u} mode, where the first term is not allowed due to selection rules. The relative intensity of the a_{2u} mode to the full Franck-Condon spectrum may be derived by noting that $Q = \sqrt{\hbar/2\omega}(a + a^\dagger)$ where a and a^\dagger are the boson annihilation and creation operators and ω is the vibration frequency. By inserting this into the Herzberg-Teller correction part in Eq. 6 we can derive the contribution of this correction (A_{HT}) to the spectrum as $\beta^2 \hbar / (2\omega)$. Therefore, the contribution of the Herzberg-Teller relative to the Franck-Condon spectrum (A_{FC}) is

$$\frac{A_{HT}}{A_{FC}} = \frac{\beta^2 \hbar}{\alpha^2 2\omega} = \frac{\beta^2}{\alpha^2} \frac{1}{2\epsilon F^2}, \quad (7)$$

where ϵ is the energy of the calculated vibration mode in eV units, Q is evaluated in $\text{amu}^{1/2} \text{\AA}$ unit and then the conversion factor $F = 15.46 \text{ C}^{1/2} \text{s}/(\text{kg} \cdot \text{m})$ ($= 10^{-10} (e \times \text{amu})^{1/2} / \hbar$). In practice, α^2 and β^2 should be determined for QL a_{2u} mode. By inspecting Eq. (6) this can be done by

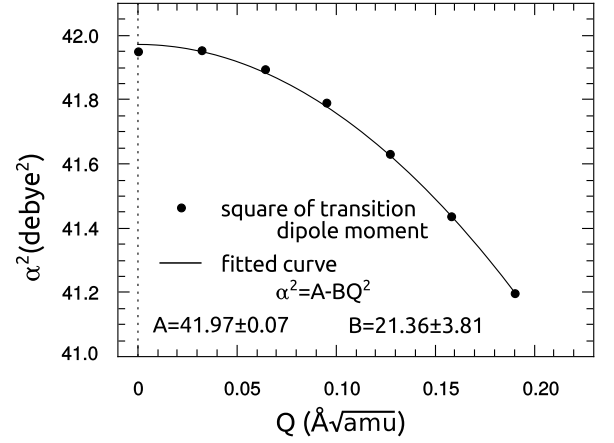


FIG. 2. Calculated absolute square of the transition dipole moment between ground and excited state (512-atom HSE06 calculations) as a function of the normal coordinate (Q) of the a_{2u} vibration mode. The straight line is a result of fitting with $A - BQ^2$ function.

calculating the absolute square of the transition dipole moment between the e_u and e_g Kohn-Sham states (representing the electronic excited and ground state, respectively, in SiV center) as a function of the atom coordinates in the supercell set by the normal coordinate of the a_{2u} mode ($Q_{a_{2u}}$). We find that the obtained plot (see Fig. 2) fits excellent to $A - BQ_{a_{2u}}^2$ function where A and B are fitting parameters. Finally, by evaluating $B/A = \beta^2/\alpha^2$ we obtained that the contribution of the a_{2u} mode to the PL spectrum with respect to the full Franck-Condon spectrum is 2.6%. This is an excellent agreement with the experimental value of $\approx 3\%$. By convolving the Franck-Condon spectrum with the Herzberg-Teller spectrum we obtain the full *ab initio* PL spectrum as the blue curve in Fig. 1(b). We prove here that the sharp feature in the PL phonon sideband indeed originates from the QL a_{2u} vibration mode where the Condon-approximation breaks down.

We further studied the effect of the isotope substitution which should change the position of the a_{2u} mode in the PL spectrum. Table I summarizes the experimental data and our results (for a method of calculation, see Supplemental Material [26]). The agreement with experiment is indeed excellent. We note that features in the spectrum at 120 and 160 meV rather come from g modes, thus they do not shift at all. This fully explains the experimental findings regarding the isotope shifts in the PL spectrum [15].

In conclusion, we implemented and tested our theory on the Herzberg-Teller effect in the PL spectrum of SiV center. We demonstrate that our approach can be very efficient to calculate the intensity of those phonons or vibrations that are otherwise are not allowed within the Franck-Condon approximation. We also showed that the phonon sideband is mostly dominated by the degenerate

TABLE I. Isotope shift of the photoluminescence (PL) phonon sideband. The isotope shift is only visible for the a_{2u} mode. In experiments (exp.) in Ref. 15, the ratio between the energy of the vibration (E_m where m is the isotope mass) varies together with the square root of the ratio of the corresponding masses that is also given in the table.

	$\sqrt{m_{29}/m_{28}}$	$\sqrt{m_{30}/m_{28}}$	E_{28}/E_{29}	E_{28}/E_{30}
exp.	1.0177	1.0357	1.016(1)	1.036(1)
theory			1.0178	1.0361

e_g phonons due to Jahn-Teller effect in SiV center. This automatically implies that the strength of the Jahn-Teller coupling so the relative intensity of the phonon sideband may be engineered by external strain in SiV center.

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